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RESEARCH MEMORANDUM

ROCKET ENGINE STARTING WITH MIXED OXIDES OF NITROGEN AND LIQUID AMMONIA BY FLOW-LINE ADDITIVES

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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SUMMARY

The starting characteristics of mixed oxides of nitrogen - liquid ammonia rocket engines were investigated with light metal additives in the ammonia flow line for ignition. The oxidant consisted of 70 percent by weight nitrogen tètroxide N_2O_4 and 30 percent nitric oxide NO. Experiments were conducted at ambient temperatures with 100- and 1000-pound-thrust engines with lithium as the additive and at -85° F with 200-pound-thrust engines with lithium, calcium, and magnesium as additives.

Starting of the engines with lithium as the additive was found to be satisfactory over a wide range of conditions. Ignition of the propellants, as evidenced by the appearance of exhaust flame, was obtained with oxidant-fuel weight ratios from 0.9 to 11 in a 100-pound-thrust engine. A 1000-pound-thrust engine was started 25 times in 25 attempts over a wide range of flow conditions, which included oxidant-fuel weight ratios from 0.6 to 14, with both oxidant and fuel flow leads, lead times from 0 to 3.4 seconds, propellant flows from 4.2 to 9.6 pounds per second, and times to reach starting flows from 0.1 to 3 seconds. With the propellants and engine at -85° F, 200-pound-thrust engines were started five times in five attempts with oxidant-fuel weight ratios from 1.1 to 4.4; operating propellant flows and chamber pressures were obtained in approximately 0.25 second. All starts were smooth except for one at an oxidant-fuel weight ratio of 4.4 where a pressure peak several times the operating pressure occurred. Eleven smooth starts were also made with the 200-pound-thrust engine for which the lithium was added to the ammonia before the runs; five of these were at -85° F, one at -50° F, and five at ambient temperature.

Experiments were also made at -85° F with calcium and magnesium as flow-line additives in 200-pound-thrust engines at oxidant-fuel weight ratios of approximately 2.0. Five smooth starts were obtained in five attempts with calcium; in three attempts with magnesium, one smooth start, one hard start, and one ignition failure resulted.

Small amounts of additive in the ammonia were found to be sufficient for engine starts but the minimum amounts required for smooth and reliable starts with the various size engines and starting conditions were not determined. Average weights of lithium in the ammonia for experiments in which smooth starts were obtained with both the 1000- and 200-pound-thrust engines were of the order of 0.05 to 0.15 percent. The 200-pound-thrust engine was started at -85° F with 0.001 pound of lithium and with 0.002 pound of calcium in a container in the ammonia flow line.

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INTRODUCTION

Since the rocket propellant combination mixed oxides of nitrogen - liquid ammonia is not spontaneously ignitible, the development of a simple and reliable engine starting method is important for its potential applications. Properties of these propellants make them well suited for storable rocket units employing pressurized-propellant-tank feed systems.

Nitrogen tetroxide N_2O_4 has many advantages as a storable oxidant. It is noncorrosive to common materials of construction, does not have an excessively high vapor pressure, and does not present serious handling problems (refs. 1, 2, and 3). It also has potentially good availability and low cost (refs. 1 and 2). Comparison of theoretical performance values with several fuels shows nitrogen tetroxide to be as good as or slightly better than nitric acid oxidizers (ref. 2). References 4, 5, and 6 give theoretical performance values of nitrogen tetroxide with various fuels. High experimental performance values have been obtained with aniline (refs. 2 and 7) and with ammonia (ref. 4) as fuels. A disadvantage of nitrogen tetroxide is its relatively high freezing point (15° F). Nitric oxide NO can be used as an additive to lower the freezing point (refs. 1 and 2); however, this has the general disadvantage of increasing the vapor pressure. The higher vapor pressure, however, is not a disadvantage for rocket applications in which the oxidant supply tank is pressurized to feed the propellant to the engine and in which the oxidant is stored in the supply tank.

Liquid ammonia, which also has a relatively high vapor pressure, is a promising fuel for use with the nitrogen tetroxide plus nitric oxide (mixed oxides of nitrogen) in such applications, because of desirable reaction properties and relatively high performance. Reference 4 gives theoretical and experimental performance values for the nitrogen tetroxide - ammonia propellant combination; experimental values of characteristic velocity and heat transfer indicated combustion efficiencies of 94 to 97 percent.

Self-igniting starting fuels and spark ignition have been used for starting with the mixed oxides of nitrogen - liquid ammonia propellant combination (ref. 4). Another starting method which has advantages for some applications is the use of an additive to the fuel which can be placed in the engine feed line. This method has been used successfully with nitric acid - ammonia (refs. 8 and 9) but has not been investigated with mixed oxides of nitrogen - ammonia, and there is no information on the starting characteristics of the combination over the wide range of starting conditions required for military use.

An experimental investigation was conducted at the NACA Lewis laboratory to determine the feasibility of starting mixed oxides of nitrogen - ammonia rocket engines with light metals as additives in the ammonia flow line. The objectives of the experiments were: (1) to determine whether reliable engine starting could be accomplished by the additive method, (2) to determine the approximate amount of additive required, and (3) to determine whether engine starts could be made by this method over a wide range of starting conditions including low temperatures, oxidant-fuel weight ratios much higher and lower than probable operating values, and either oxidant or fuel flow leads.

An oxidant consisting of 70 percent nitrogen tetroxide and 30 percent nitric oxide was used for the engine starting experiments; the freezing point of this mixture is approximately -110° F (ref. 2), which is safely below that expected in use. Investigations were made at ambient temperatures on 100- and 1000-pound-thrust engines with lithium as the additive and at low temperatures with lithium, calcium, and magnesium as additives. Ignition was first investigated in the 100-pound-thrust engine at oxidant-fuel weight ratios from 0.9 to 17 (stoichiometric ratio is 2.18). Starting experiments were then made on the 1000-pound-thrust engine with oxidant-fuel weight ratios from 0.6 to 14, with both oxidant and fuel flow leads, and with initial total flow rates from 4.2 to 9.6 pounds per second. With both the propellants and engine assembly at temperatures as low as -85° F, starting experiments were made with the 200-pound-thrust engine; oxidant-fuel weight ratios for these experiments were 1.1 to 4.4, and initial flow rates were 1.0 to 1.3 pounds per second.

APPARATUS AND PROCEDURE

Three different setups were used in the investigation. Experiments at ambient temperatures were made with engines of approximately 100 and 1000 pounds thrust; at low temperatures, 200-pound-thrust engines were used. The oxidant and fuel were the same in all cases. The oxidant consisted of 70 percent nitrogen tetroxide and 30 percent nitric oxide by weight, and the fuel was commercial anhydrous liquid ammonia. The

lithium additive was stored in mineral oil; some oxidation probably occurred in handling prior to its use as an additive.

100-Pound-Thrust Facility

Flow system. - A schematic sketch of the flow system for the 100-pound-thrust facility is shown in figure 1. The system consisted of the fuel and oxidant supply tanks, equipment for pressurizing the tanks with nitrogen gas, flow lines, remotely operated valves for controlling propellant flows, a lithium container in the fuel line, and the engine assembly. The pressures in the oxidant and fuel tanks were individually controlled by separate nitrogen gas regulators. 2923

Engine assembly. - The 100-pound-thrust engine (fig. 2) consisted of propellant injector, combustion chamber, and exhaust nozzle. The propellant injector had one fuel orifice in the center and four oxidant orifices. Four oxidant jets impinged on the center fuel jet approximately 5/16 inch from the fuel outlet. The size of the oxidant orifices was the same for all experiments, but the diameter of the fuel orifice was 0.059 inch for the first 44 runs and 0.078 inch for runs 45 to 67. The combustion chamber, which was sealed to the propellant injector by means of a flange, was a steel tube 1/4 inch thick, 8 inches in length, and 2 inches in inside diameter. The nozzle was made of aluminum and had a convergent half angle of 60° and throat diameter of 0.557 inch. The first 32 runs were made without the exhaust nozzle and with a combustion chamber similar to the one shown in the sketch, but 32 inches in length.

Lithium containers. - The lithium container is shown in figure 3. For design A the inner cylinder was made of stainless-steel screen and for design B the cylinder was made of stainless-steel sheet, except for a metal screen outlet facing the outlet tube on the housing.

Instrumentation. - Oxidant and fuel flows before combustion were determined from the pressure differentials between the supply tanks and the atmospheric pressure in the combustion chamber by means of flow coefficients which were obtained for each flow system by calibrations with water. Pressures in the supply tanks were measured within ±5 pounds per square inch by Bourdon gages. The accuracy of the flow determinations was estimated to be within ±5 percent. Chamber pressures were measured within ±5 pounds per square inch by a Bourdon type pressure recorder.

The amounts of lithium were weighed on balances within 1 percent; however, the actual weights of lithium were probably as much as 5 percent less than those measured because the lithium during weighing was protected from the atmosphere by a light covering of oil.

Procedure. - The lithium was prepared by scraping chips from a solid block (about 20 chips per gram); the material was protected from the atmosphere with mineral oil. After the oxidant and fuel were loaded into the supply tanks, the lithium chips were placed in the container and the protective oil film was removed. The supply tanks were then pressurized with nitrogen gas and regulators were preset to maintain the tanks at desired pressures. Valves were then opened which allowed the propellants to flow to the combustion chamber. The exhaust was observed for the appearance of flame and a gage was observed to measure chamber pressure. When no combustion occurred, the flows were maintained for approximately 2 to 3 seconds; when combustion occurred, the flows were maintained long enough to observe the exhaust flame and obtain a steady combustion-chamber pressure record (from 2 to 5 sec).

1000-Pound-Thrust Facility

Flow system. - The flow system for the 1000-pound-thrust facility is shown in figure 4. The system was similar to the 100-pound-thrust facility, but used larger equipment and had orifices in the flow lines to measure propellant flows and equipment to purge the engine with high-pressure helium gas. The lithium container was located in the fuel line approximately 1 foot upstream of the injector.

Engine. - Figure 5 is a sketch of the 1000-pound-thrust engine assembly which consisted of the propellant injector, combustion chamber, and exhaust nozzle. The propellant injector consisted of 24 fuel and 48 oxidant orifices arranged to result in 24 sets of triplet-pattern impinging jets, equally spaced about a circle. Two oxidant jets and a single fuel jet impinged approximately 1/4 inch from the orifices. The combustion chamber was an uncooled steel tube with a chrome-plated inner surface; it was 12.3 inches long and the walls were 1/2 inch thick. The nozzle was of solid copper with a chrome-plated inner surface and a throat diameter of 1.841 inches. This nozzle was designed to expand the propellant gases to atmospheric pressure with a chamber pressure of 300 pounds per square inch; the engine developed approximately 1000 pounds thrust at that condition. The characteristic length L^* of the engine was 63 inches.

Lithium container. - The lithium container was similar to that used for most of the experiments with the 100-pound-thrust engine except for larger (5/8-in. diam.) inlet and outlet tubes. The inner container was design B as shown in figure 3.

Instrumentation. - Propellant flows were measured by orifices in the oxidant and fuel lines between the supply tanks and control valves (fig. 4). The pressure differentials for these orifices were measured continuously during a run by means of transducers and a recording oscillograph. The accuracy of the flow measurements varied because of the

large flow ranges; flows were measured within approximately ±3 percent at oxidant-fuel ratios less than 8; for ratios greater than 8, the fuel flows were very small and were measured within approximately ±8 percent. The accuracies of the flow measurements were considered sufficient for starting experiments even with the variations described. Flow measurements were also obtained for several runs by continuous weighing of the propellant supply tanks by the use of strain gages. In order to obtain measurements within ±2 percent by this method, approximately 3 seconds or more of steady flow was required.

Pressures in the engine combustion chamber and in the propellant flow lines immediately upstream of the propellant injector were measured within approximately ±15 pounds per square inch by pressure transducers and a recording oscillograph.

Weights of lithium were obtained in the same manner as described for the 100-pound-thrust engine.

Procedure. - The propellants were loaded into the tanks and the lithium was prepared, weighed, and placed into the container as described for the 100-pound-thrust engine. The propellant tanks were then pressurized, the helium regulators were preset to maintain the tanks at desired pressures, and pneumatic and electric controls for the throttling valves were set to result in desired starting flow conditions. The valve controls were then energized to allow starting flows into the engine. When the starting flows resulted in high combustion pressure, the engine was run for about 5 seconds without a change in the flow controls. When the starting flows resulted in relatively low combustion pressure, the flow controls were changed after the engine start to result in a higher combustion pressure.

Low-Temperature Test Facility

Flow system. - The flow system for the 200-pound-thrust low-temperature facility is shown in figure 6. The system was similar to the 1000-pound-thrust facility, but smaller equipment was used and the engine exhausted into a large tank. The fuel and oxidant control valves were both operated by a single actuating mechanism. The lithium container was located 2 inches upstream of the propellant injector.

Refrigeration system. - For cold runs, the entire rocket assembly including engine, valves, flow lines, and tanks was submerged in a tank filled with alcohol. Constant temperature was maintained by circulating the alcohol through a system consisting of a warm bath (water) and a cold bath (dry ice and alcohol), mixing valves, and a controller (ref. 10).

Engines. - Two engine assemblies were used for the experiments. Engine A (fig. 7) consisted of the propellant injector and a one-piece aluminum combustion chamber and nozzle. The characteristic length L^* of the engine was approximately 50. The propellant injector for engine B was similar to that for engine A; however, the dimensions were slightly different so as to fit a combustion chamber with an inside diameter of 1.88 inches, and the exhaust nozzle was separate. The combustion chamber was 3.75 inches long with 1/8-inch-thick steel walls and the nozzle had thick steel walls. Since severe erosion caused the nozzle throat to change continuously during the experiments, the characteristic length could not be determined.

Additive container. - The container for the metallic additives is shown in figure 8.

Instrumentation. - Propellant flows were measured continuously during a run within ±5 percent by means of orifices, differential pressure transducers, and a recording oscillograph.

Pressures in the engine combustion chamber and in the propellant flow lines immediately upstream of the propellant injector were measured within approximately ±10 pounds per square inch by pressure transducers and a recording oscillograph.

The propellant valve position was converted to electrical voltage by means of a rack and pinion operating a variable resistance; the readings were continuously recorded by an oscillograph.

Temperatures were measured within $\pm 2^{\circ}$ F by thermocouples immersed in the propellants in the supply tanks and by two thermocouples in the coolant bath.

Procedure. - Two different procedures were used for the addition of the lithium to the fuel. For one procedure, the propellants were loaded into the tanks and the lithium was prepared, weighed, and placed into the container in the flow line in the manner described for the experiments on the other setups except that the protective oil covering was not removed. For the other procedure, the oxidant was first loaded and then lithium was placed in a container in the line through which the ammonia was loaded such that lithium was dissolved by the ammonia flow during the loading of the tank.

For all the runs with calcium and magnesium, the additives were placed in the container in the engine flow line. The calcium was in the form of coarse turnings which were used as received from the supplier; the surfaces were not protected from the atmosphere. The magnesium was in the form of wire approximately 1/8 inch in diameter; the surfaces were cleaned with an abrasive and protected from the atmosphere with oil.

After the propellants were loaded, the engine was ready for firing for runs at ambient temperatures; for the low-temperature runs, refrigerant was circulated through the coolant bath and sufficient time was allowed for all thermocouples to reach the desired low temperature within 1° or 2° F. Gas regulators were then set and the tanks pressurized to give the desired flow rates. The propellant valves were opened and the engine was fired until the propellants were exhausted.

RESULTS AND DISCUSSION

Ignition Experiments With 100-Pound-Thrust Engine

Preliminary experiments with open tube. - The first series of 32 runs, which was very preliminary in nature, was made without the nozzle to determine whether lithium in ammonia would ignite spontaneously with the mixed oxides of nitrogen. Initial flow varied from 0.2 to 0.5 pound per second and mixture ratios from 2.3 to 4.6. The appearance of flame was used as a criterion of ignition. Two runs without lithium showed no flame. Of 27 runs made with lithium in container A (fig. 3), only four showed flame. For the four runs in which ignition was obtained, ammonia was left in contact with the lithium for several minutes before the run, which resulted in a lithium-rich slug of ammonia in the container before flow was started and the oxidant flow led into the chamber. When fuel flow led into the chamber, the lithium-rich slug was probably exhausted before the oxidant flow started and no ignition resulted.

In order to achieve better contact of ammonia with lithium during flow, the container was modified so that all the ammonia was forced over the lithium (fig. 3, design B). Ignitions were obtained in each of three runs made with the modified container. These ignitions were the result of lithium dissolving in the ammonia during flow through the container because ammonia was not in contact with the lithium before the runs and, for two of the runs, fuel flow led into the chamber.

Experiments with 100-pound-thrust engine. - Ignition experiments, primarily to determine if flame occurred over a wide range of mixture ratios, were made with the 100-pound-thrust engine. During the runs, other factors affecting ignition were considered such as amount of lithium, flow rates, and prior condition of engine and flow system (whether the engine was warm or cold, and possibility of additive deposits). The results are shown by table I in the order in which the runs were made.

With the engine at ambient temperature, ignitions were obtained with oxidant-fuel ratios from 0.9 to 11 (runs 33, 40, 49, 58, 59, and 67). An exception to this range of mixture ratio for which ignition was obtained occurred for run 45 at an oxidant-fuel ratio of 1.0 with a small amount of lithium. It was also noted that a comparatively large

amount of lithium was required to obtain ignition at high oxidant-fuel ratios (5 and above). For example, in run 33 where ignition occurred at an oxidant-fuel ratio of 11, the container was full (0.044 lb); with smaller amounts of lithium in the container (0.01 lb or less), no ignitions occurred at oxidant-fuel ratios of 5 and higher (runs 60 to 66).

With the engine warm from previous combustion, ignitions were obtained at mixture ratios from 0.9 to 8 (runs 34 to 37, 41, 44, and 46 to 48). No ignition occurred at oxidant-fuel ratios of 15 and 17 (runs 42 and 43). Also, no ignition was observed for two runs near stoichiometric (runs 38 and 39); this was apparently caused by lack of lithium because the container was removed after the runs and found to be empty.

With a warm engine, it was found that ignitions occurred without lithium in the container probably because of deposits in the flow system which resulted from the use of lithium during previous runs; ignitions were obtained under these conditions at mixture ratios from 0.9 to 10.4 (runs 50 to 54). When the lines were cleaned, no ignition occurred (run 55); at the same operating conditions but with a very small amount of lithium (0.00027 lb), ignition occurred (run 58).

The results of runs 56 and 57 indicated that without additive, and at a high mixture ratio (approximately 10), a warm engine could cause enough reaction to result in chamber pressure but not ignition (flame). Both runs were made at approximately the same conditions, without lithium in the container and with the flow sytem cleaned of deposits; no chamber pressure was obtained with the engine at ambient temperature but 45 pounds per square inch gage was obtained with the warm engine.

Discussion on amounts of additive used. - The amount of lithium used per run was in the range 0.05 to 0.15 percent of the amount of ammonia used. Although the minimum amounts of lithium required for ignition were not determined, it is of interest to note that ignitions were obtained for many of the runs with less than 0.01 pound of lithium in the flow-line container and that deposits in the flow system alone were sometimes sufficient to cause ignition.

The experiments indicated that ignition occurred more readily in the engine than in the open tube. This is based on a comparison of experiments where it would be expected that as much lithium was dissolved in the ammonia in one case as in the other.

1000-Pound-Thrust Engine Experiments

Experiments were conducted with a 1000-pound-thrust engine to determine the starting characteristics with various flow conditions with

lithium added to the ammonia in the flow line. Table II shows the results of 25 starts, all of which were successful; no damaging hard starts occurred.

Typical data record. - In order to clarify the data of table II, the data from a typical run will be discussed. Figure 9 shows an oscillograph-time record of chamber pressure, fuel and oxidant injection pressures, and fuel and oxidant orifice differential pressures for run 8. Run 8 was made with an oxidant lead and with a high oxidant-fuel ratio. Zero time on the record is for energizing of the electrical circuit which controlled the opening of the propellant valves. The oxidant flow was first to start (as indicated by orifice differential pressure) and oxidant injection pressure rose rapidly a fraction of a second later. This relation between flows and injection pressures existed because the orifices were located upstream of the injector pressure taps; flows therefore passed the orifices before the pressure at the injector rose. A slow rise in fuel flow then occurred, followed by a small increase in fuel injection pressure. Fuel injection and chamber pressure then increased very rapidly, at the same time, to relatively high values.

The record indicates that when the fuel control valve started opening, the fuel flow was initially very small and that an appreciable time was required to fill the flow line before fuel reached the injector. The pressure at the injector then increased rapidly, fuel flowed into the chamber, and combustion pressure rose. The slight indication of fuel injection pressure prior to the time of rapid rise was probably caused by pressure in the combustion chamber resulting from the high oxidant flow.

For the starting flow conditions, the lead time for oxidant flow was taken between the rise of oxidant and fuel injection pressures, and the times required to obtain starting propellant flows were taken from the initial rise to full flow. Propellant flow and mixture ratio were taken at the time the lagging propellant reached full flow. The chamber pressure resulting from the starting flows was the highest pressure reached before flows were changed to give higher thrust. The record shows that chamber pressure increased rapidly at first to about 180 pounds per square inch, and then, although propellant flows remained constant, the pressure increased about 60 pounds per square inch during the following second. This was characteristic of runs in which the starting mixture ratio was very high.

The fuel control valve was then further opened and the record shows an increase of fuel injector pressure, fuel flow, and chamber pressure and a resulting decrease of oxidant flow. Data for the conditions after the flow change to higher thrust were taken where the oxidant and fuel flows were constant, at the highest chamber pressure.

Starting variables. - As shown by table II, starting flow conditions included oxidant-fuel flow ratios from 0.6 to 14, both oxidant and fuel flow leads, lead times from 0 to 3.4 seconds, and propellant flows from 4.2 to 9.6 pounds per second. Times required to obtain the starting propellant flows (start of flow to full flow) varied from 0.1 to 3 seconds. The lithium container was located in the fuel line downstream of the control valve and 12 inches upstream of the propellant injector (fig. 4). The ammonia was therefore not in contact with the lithium until flow to the engine was started.

For runs in which the starting flows and flow ratios resulted in a relatively low chamber pressure, the flows were changed after the start for operation at higher thrust in order to demonstrate more fully a complete engine start; these conditions are also shown by table II. Exhaust flame was observed with the starting flows in all runs except for a few at the highest mixture ratios. There was smooth transition to higher thrust in every run when the flows were changed.

Although the runs were made primarily for starting, an attempt was made to obtain performance in seven of the runs by operating long enough to use continuous propellant tank weighing. The data obtained show very high values of characteristic velocity and, except for two runs, low values of specific impulse. Based on the theoretical performance of nitrogen tetroxide and ammonia at 500 pounds per square inch (ref. 4) which approximates that for the propellants used, some of the characteristic velocities were higher than theoretical; specific impulse values ranged from 70 to 100 percent of theoretical with only two of the values above 86 percent of theoretical.

Amounts of lithium. - Amounts of lithium in the container for runs in which this was known are shown in table II. In most cases the container was filled (0.044 pound) and a series of runs was made without adding lithium or removing the container (see table II). It was also possible to start the engine without lithium in the container as was observed during the ignition experiments with the 100-pound-thrust engine. Two such starts were made probably as the result of deposits in the flow system resulting from the use of lithium during previous runs. Before run 10, many runs had been made with lithium, but the engine had not been operated for several days. During this time, the flow system was vented to the atmosphere; the fuel flow line was coated with white deposits. With the lithium container left out of the flow line, the engine started with high propellant flows at a mixture ratio of 2.1. Run 22 was also made without the lithium container following a series of runs in which lithium was used; the engine started with high flows at a mixture ratio of 3.1.

The average weight of lithium in ammonia for the experiments was in the order of 0.05 to 0.1 percent; values were obtained by dividing the amount of lithium dissolved by the total flow of ammonia for a series of runs.

Low-Temperature Experiments

The starting characteristics of a 200-pound-thrust engine were investigated at low temperatures with lithium, calcium, and magnesium as additives. The additives were used in the ammonia flow line in the same manner as the lithium in the other engines. Experiments were also conducted in which the lithium was added to the ammonia when it was loaded into the supply tank.

Lithium added in flow line. - Five engine starts were obtained in five attempts with the engine and propellants at -85° F and with lithium placed in the flow line container as shown in figure 6. The low-temperature test facility was employed with engine assembly A (fig. 7); the data for the runs are shown by table III. Figure 10 shows an oscillograph-time record of the valve position, oxidant and fuel injection pressures, oxidant and fuel orifice differential pressures, and chamber pressure for run 2; the record is typical of those obtained for the other runs. The record shows that the build-up of injection pressures, flows, and chamber pressure all followed one another very closely and reached their approximate operating values in 0.3 second. After this time the different values adjusted somewhat and the chamber pressure increased about 60 pounds per square inch.

The data for the runs show mixture ratios from 1.1 to 4.4, total propellant flows from 1.0 to 1.2 pounds per second, times to obtain starting propellant flows of 0.2 to 0.3 second, and chamber pressures from 340 to 443 pounds per square inch.

The rise of chamber pressure followed closely the rise of the propellant flows for each start. The time required to reach high propellant flows was approximately the same for all runs (0.2 to 0.3 sec); the time required for full valve opening varied from 0.02 to 0.5 second. In contrast to these rapid valve openings, data reported in reference 10 show that valve opening times greater than 1.5 seconds were required to obtain ignitions of nitric acid with 70 percent triethylamine - 30 percent orthotoluidine as fuel at -85° F with similar apparatus.

For runs 1 to 4, for which the mixture ratio varied between 1.1 and 2.4, the chamber pressure records showed no evidences of overpressure during the starts (pressure peaks higher than operating pressure). For run 5, in which the mixture ratio was 4.4, the chamber pressure record

showed that an instantaneous high pressure peak occurred during the normal pressure rise at the start; the pressure reached could not be determined from the record. The remainder of the run was normal as with the other runs. Examination of the thin-wall aluminum engine after the run showed it to be stretched as a result of the high pressure, which must have reached several times operating pressure. This one run indicated that possible difficulty with hard starting may be encountered at extremely low temperature (-85° F) and high mixture ratio (4.4); it is possible that the difficulty may be eliminated by the use of larger amounts of lithium.

Although measurements of flows and pressures were not accurate enough to determine reliable performance values, the data obtained indicate that characteristic velocities were only in the order of 70 to 85 percent of theoretical values.

The amounts of lithium used varied from 0.0011 to 0.0022 pound and little or no lithium was left in the container after the runs. The average weight of lithium in the ammonia during each of the runs was less than 0.1 percent.

<u>Lithium added to the ammonia before runs</u>. - Eleven starts were also obtained in runs for which the lithium was dissolved by the ammonia as it was loaded into the supply tank. Five of these runs were made with engine and propellants at -85° F, one at -50° F, and five with the engine and oxidant at room temperature and the fuel at +10° to -20° F. The weight of lithium dissolved by the ammonia for these runs was of the order of 0.1 percent.

Data for the runs are shown in table IV; mixture ratios varied from 1.4 to 1.8, propellant flows from 1.1 to 1.3 pounds per second, valve opening times from 0.2 to 3 seconds, and chamber pressures from 72 to 420 pounds per square inch. Both engines A and B (described in the APPARATUS) were used during the series of runs.

Data on the times required to reach high propellant flows and high chamber pressure are presented in table IV; comparison of these values shows that in most cases the rise of chamber pressure followed closely the rise of propellant flows. The flows and pressures reached in the times given were not the highest for the runs but represent the starting period during which nearly peak values were reached; flows and pressures changed somewhat after the start and the pressures given in the table were the highest obtained during the run.

Flow rates were not obtained for the runs with engine A, and with engine B the area of the nozzle throat was unknown because of continuous erosion during the runs; therefore, it was not know whether the combustion pressures obtained indicated high combustion efficiencies. For

the runs with engine B the chamber pressures tended to decrease from one run to the next as the nozzle throat enlarged because of severe erosion. The low pressures of the last two runs were probably due to this decrease and also to lower propellant flows (after the runs, the injector orifices were found to be partly blocked by solid deposits).

Results without additive and with calcium and magnesium added in flow line. - A brief series of experiments was made at -85° F to further investigate ignition of the propellants and to investigate other additives which for logistic reasons might be desirable substitutes for lithium. All the runs were made with engine A (fig. 7) at mixture ratios of approximately 2.0 (additives were placed in the container in the engine flow line); the results are shown in the following table:

Additive	Smooth starts	Hard starts	No ignition
None (nitric acid flush before run)	1	1	0
None	0	1[a]	5
Calcium	5	0	0
Magnesium	1	1	1

[a]Explosion.

Before two of the eight runs without additive in the flow line container, the fuel flow system was cleaned and also flushed with nitric acid in order to remove any deposits which may have remained from previous runs with additive. Engine starts were obtained in both runs: one was a smooth start, but the other was a hard start which stretched the engine walls. Of the other six runs without additive, three were made following one of the runs for which the acid flush was used and the other three runs were made following the other run in which acid flush was used. Engine starts were not obtained for any of the six runs; five resulted in no ignition and the other in an explosion which damaged engine and setup. The reason for the engine starts after the acid flush is not known; one possibility is that the surfaces of aluminum fittings in the flow line were cleaned and aluminum acted as a catalyst.

Five runs were made with approximately 0.002 to 0.003 pound of calcium in the flow line container; smooth starts (similar to those obtained with lithium) were obtained in each run. The fuel flow system

was cleaned before the experiments. All the calcium in the container was dissolved by the ammonia flow during each run. These results indicate that calcium may be a suitable flow-line additive as was shown for lithium by extensive experiments.

Three runs were made with approximately 0.004 pound of magnesium in the flow-line container; before the runs the fuel flow system was cleaned. The results of these runs were varied: one smooth start, one hard start, and one ignition failure were obtained. No difference in the weight of the magnesium before and after the runs could be detected; if magnesium was dissolved during the run it was slight and was of the same order of magnitude as the weight of the oil covering on the magnesium. These results indicated the possibility that a trace amount of magnesium may be sufficient to cause ignition but that magnesium would probably not be a suitable additive in the flow line because of its low solubility in ammonia.

In general, the results of the experiments shown in the table indicate that small traces of additive were sufficient to result in ignition of the propellants but that in order to achieve reliable and smooth engine starts a sufficient amount of effective additive must be dissolved in the ammonia.

Discussion

Small quantities of additives were sufficient to result in spontaneous ignition of the propellants during the experiments. This indicates that the ignitions were the result of a catalytic effect of the additives.

For runs in which lithium was used the catalytic effect was probably produced by the lithium in solution. It has been found that alkali metals do not tend to react with cold ammonia (ref. 11, p. 622) and the short times that the solutions were in the flow system reduced the possibility for lithium - ammonia reaction which is promoted by metal surfaces. The ammonia was at approximately 0° F for the runs at ambient temperature (because of the method used to transfer it to the engine tank) and at -85° F for the low-temperature experiments.

It is probable that many additives other than those investigated could be used in the ammonia flow line to obtain engine starting. Several of the other alkali and alkaline earth metals would probably be better qualified logistically than is lithium. Calcium has advantages over lithium on the basis of availability, cost, and ease of handling, and the results of the starting experiments at -85° F indicate that it may be a satisfactory additive.

In practice, there are many ways in which additives could be used for ignition purposes; the most suitable would depend on the additive used and the application. If it were desired to use lithium in the fuel flow line for a storable rocket unit, the lithium could be protected from the atmosphere by various means such as diaphrams which would burst when the fuel flowed. The present investigation indicates that other suitable additives, for example, calcium, may not require so much protection from the atmosphere; they could be used in the flow line in a manner similar to that used in the experiments of this report. It may also be desirable for some applications to seek a catalyst which could be added to one of the propellants before storage.

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SUMMARY OF RESULTS

The following results were obtained in an investigation of starting mixed oxides of nitrogen - ammonia rocket engines with light metal additives. The oxidant consisted of 70 percent by weight nitrogen tetroxide and 30 percent nitric oxide. The additives were placed in a container in the ammonia feed line a short distance upstream of the injector. The experiments were conducted at ambient temperatures with 100- and 1000-pound thrust engines with lithium as additive and at -85° F with 200-pound-thrust engines with lithium, calcium, and magnesium as additives.

1. Engines were started over a wide range of conditions with lithium as the additive.

2. Ignitions as evidenced by exhaust flames were obtained with lithium as the additive in the 100-pound-thrust engine at oxidant-fuel weight ratios from about 0.9 to 11.

3. The 1000-pound-thrust engine was started 25 times over a wide range of flow conditions without the occurrence of any damaging hard starts with lithium as the additive. The starts were made with oxidant-fuel weight ratios from 0.6 to 14, both oxidant and fuel flow leads, lead times from 0 to 3.4 seconds, propellant flows from 4.2 to 9.6 pounds per second, and times to reach starting flows from 0.1 to 3 seconds.

4. The 200-pound-thrust engine was started with the propellants and engine assembly at -85° F. Five such starts were obtained out of five attempts with lithium at oxidant-fuel weight ratios from 1.1 to 4.4; operating propellant flows and chamber pressure were obtained in approximately 0.25 second. All the starts were smooth except for one at an oxidant-fuel weight ratio of 4.4; a pressure peak several times the operating pressure occurred during that start.

5. Eleven smooth starts were also made with the 200-pound-thrust engine for which the lithium was added to the ammonia before the runs. Five of these runs were at -85° F, one at -50° F, and five at room temperature.

6. Five smooth starts were also obtained with the 200-pound-thrust engine and propellants at -85° F with calcium as the additive in the flow line at oxidant-fuel weight ratios of approximately 2.0. Results with magnesium as additive at the same conditions were varied; one smooth start, one hard start, and one ignition failure were obtained.

7. Amounts of additive required for starting were small; however, the minimum amounts required for smooth and reliable starts with the different size engines and various starting conditions were not determined. The following results illustrate some small amounts of additive used successfully:

(a) Ignition was obtained in the 100-pound-thrust engine with as little as 0.0003 pound lithium in the flow-line container.

(b) The 200-pound-thrust engine was started at -85° F with 0.001 pound of lithium and with 0.002 pound of calcium in the container.

(c) The 100- and 1000-pound-thrust engines started without additive in the container probably because of deposits in the flow system resulting from the use of lithium during previous runs.

(d) The average weights of lithium in ammonia were of the order of 0.05 to 0.15 percent.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, April 27, 1953

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TABLE I. - IGNITION EXPERIMENTS WITH 100-POUND-THRUST ENGINE

WITH DESIGN B LITHIUM CONTAINER

Run	Lithium in container, lb	Engine temperature[a]	Starting propellant flow, lb/sec	Starting oxidant-fuel weight ratio	Chamber pressure, lb/sq in. gage	Ignition (b)
33	[c]0.044	C	0.47	11.0	45	F
34	↓	W	.34	6.5	20	F
35	↓	W	.38	6.8	25	F
36	↓	W	.38	7.9	15	F
37	↓	W	.35	1.9	30	F
38	↓	W	.38	1.7	0	-
39	↓	W	.35	1.9	0	-
40	[c]0.044	C	0.56	2.7	140	F
41	↓	W	.40	1.6	50	F
42	↓	W	.78	17.0	30	-
43	↓	W	.79	15.0	50	-
44	↓	W	.39	1.6	40	F
45	[c]0.004	C	0.51	1.0	60	-
46	↓	W	.39	1.8	60	F
47	↓	W	.53	1.0	70	F
48	↓	W	.49	.9	55	F
49	0.00055	C	0.49	0.9	35	F
50	0	W	0.49	0.9	30	F
51	0	W	.79	2.1	250	F
52	0	W	.81	10.4	40	F
53	0	W	.79	2.1	250	F
54	0	W	.79	2.1	125	F
55	[d]0	C	0.77	2.0	70	-
56	0	W	.82	9.5	45	-
57	0	C	.81	10.4	0	-
58	0.00027	C	0.78	2.0	195	F
59	0	C	0.77	2.0	225	F
60	0.00013	C	0.80	12.5	0	-
61	[c]0.01	C	0.81	11.0	0	-
62	↓	C	.83	8.0	0	-
63	↓	C	.84	7.6	0	-
64	0.01	C	0.84	7.4	0	-
65	[c]0.01	C	0.85	6.9	100	-
66	↓	C	.85	6.6	105	-
67	0.01	C	0.89	4.9	210	F

[a]C denotes ambient; W above ambient.

[b]F signifies exhaust flame.

[c]Initial weight in container for series of runs with one loading; arrow indicates runs of the series.

[d]Before run 55 the fuel flow system was cleaned of deposits resulting from the use of lithium.

TABLE II. - DATA FOR STARTING EXPERIMENTS WITH 1000-POUND-THRUST ENGINE

Run	Lithium in container, lb	Starting flow conditions							Conditions after flow change		
		Propellant flow leading	Lead time, sec	Time to reach starting flows, sec		Total propellant flow, lb/sec	Oxidant-fuel weight ratio	Chamber pressure, lb/sq in. gage	Total propellant flow, lb/sec	Oxidant-fuel weight ratio	Chamber pressure, lb/sq in. gage
				Fuel	Oxidant						
1	[a]0.044	Oxidant	0	0.9	1.2	[c]7.8	[c]2.4	434	---	---	---
2	↓	Oxidant	.3	1.0	1.2	[c]6.5	[c]1.7	438	---	---	---
3	↓	Oxidant	.2	.9	1.2	[c]5.9	[c]1.2	380	---	---	---
4	[a]0.044	Fuel	1.0	---	1.65	7.4	1.1	295	6.8	1.5	414
5	↓	Oxidant	2.1	2.0	.8	9.4	13	150	---	---	---
6	↓	Oxidant	1.8	1.7	.7	8.0	8.7	260	8.0	4.8	342
7	↓	Fuel	1.7	1.0	1.9	7.1	1.2	155	6.6	1.6	421
8	↓	Oxidant	1.5	1.8	.8	9.6	14	240	9.2	5.7	368
9	↓	Oxidant	1.2	3.5	.8	7.5	8.4	178	7.8	3.9	366
10	0	Fuel	0.3	1.1	1.2	[c]8.6	[c]2.1	470	---	---	---
11	[a]0.0088	Oxidant	2.4	2.4	0.6	9.4	14	200	7.1	4.3	360
12	↓	Fuel	1.4	1.0	2.6	6.5	1.0	280	7.0	1.6	318
13	0.0044	Fuel	1.7	1.0	1.8	6.3	1.0	220	---	---	---
14	0.018	Fuel	3.4	1.2	3.0	5.3	0.9	270	---	---	---
15	[a]0.044	Oxidant	0.9	0.3	0.5	9.6	1.4	242	6.5	1.4	378
16	↓	Oxidant	2.1	.4	.25	8.6	15	110	6.9	4.8	298
17	↓	Fuel	.4	.4	.07	4.2	.6	162	6.0	1.8	326
18	↓	Fuel	.5	.4	---	[b]8.2	[b]14	115	---	---	150
19	↓	Fuel	.6	.3	.1	7.7	14	110	---	---	---
20	↓	Fuel	.6	.4	.5	8.7	13	95	6.6	3.3	260
21	↓	Fuel	.4	.4	.2	4.6	1.5	285	---	---	---
22	0	Oxidant	0.25	0.4	0.4	[c]8.7	[c]3.1	394	---	---	---
23	[a]0.013	[b]Oxidant	----	---	0.5	[c]6.4	[c]1.6	365	---	---	---
24	↓	[b]Oxidant	----	---	.4	[c]6.0	[c]1.4	354	---	---	---
25	↓	[b]Oxidant	----	---	.1	5.5	1.3	335	---	---	---

[a]Initial weight in container for series of runs with one loading; arrow indicates runs of the series.
[b]No instrument record obtained; values estimated from records of other runs with same flow settings.
[c]Determined by continuous weighing during run.

TABLE III. - DATA FOR EXPERIMENTS WITH ENGINE AND PROPELLANTS AT -85° F AND LITHIUM IN ENGINE FLOW LINE

[200-Pound-thrust engine A.]

Run	Lithium in container, lb	Propellant flow, lb/sec	Time for full valve opening, sec	Time from injection pressure rise to high flows, sec	Time from injection pressure rise to high chamber pressure, sec	Oxidant-fuel weight ratio	Chamber pressure, lb/sq in. gage
1	0.0020	1.0	0.50	0.3	0.3	2.4	340
2	.0022	1.1	.02	.2	.2	1.4	443
3	.0018	1.1	.12	.25	.25	1.4	440
4	.0011	1.1	.08	.25	.25	1.1	365
5	.0022	1.2	.30	.3	.4	4.4	360

TABLE IV. - DATA FOR EXPERIMENTS WITH LITHIUM ADDED TO AMMONIA BEFORE RUNS

[200-Pound-thrust engines A and B.]

Run	Propellant temperatures, °F		Propellant flow, lb/sec	Time for full valve opening, sec	Time from injection pressure rise to high flows, sec	Time from injection pressure rise to high chamber pressure, sec	Oxidant-fuel weight ratio	Highest chamber pressure reached, lb/sq in. gage
	Fuel	Oxidant						
6	10	55	---	2.2	0.6	0.6	---	295
7	-20	55	---	3.0	1.0	1.0	---	265
8	0	45	---	1.6	1.1	1.1	---	310
9	0	40	1.1	2.4	.8	1.0	1.8	334
10	25	52	1.1	2.5	.8	1.1	1.6	420
11	-50	-58	[a]1.3	1.7	.6	.6	[a]1.8	370
12	-84	-84	1.3	2.4	.5	.6	1.5	215
13	-85	-85	1.1	---	.3	.5	1.4	240
14	-84	-84	1.3	---	.7	.9	1.5	197
15	-85	-85	---	[a].2	.3	.4	---	72
16	-85	-85	---	[a].2	---	.4	---	81

[a]No instrument record obtained; values estimated from records of other runs with same flow settings.

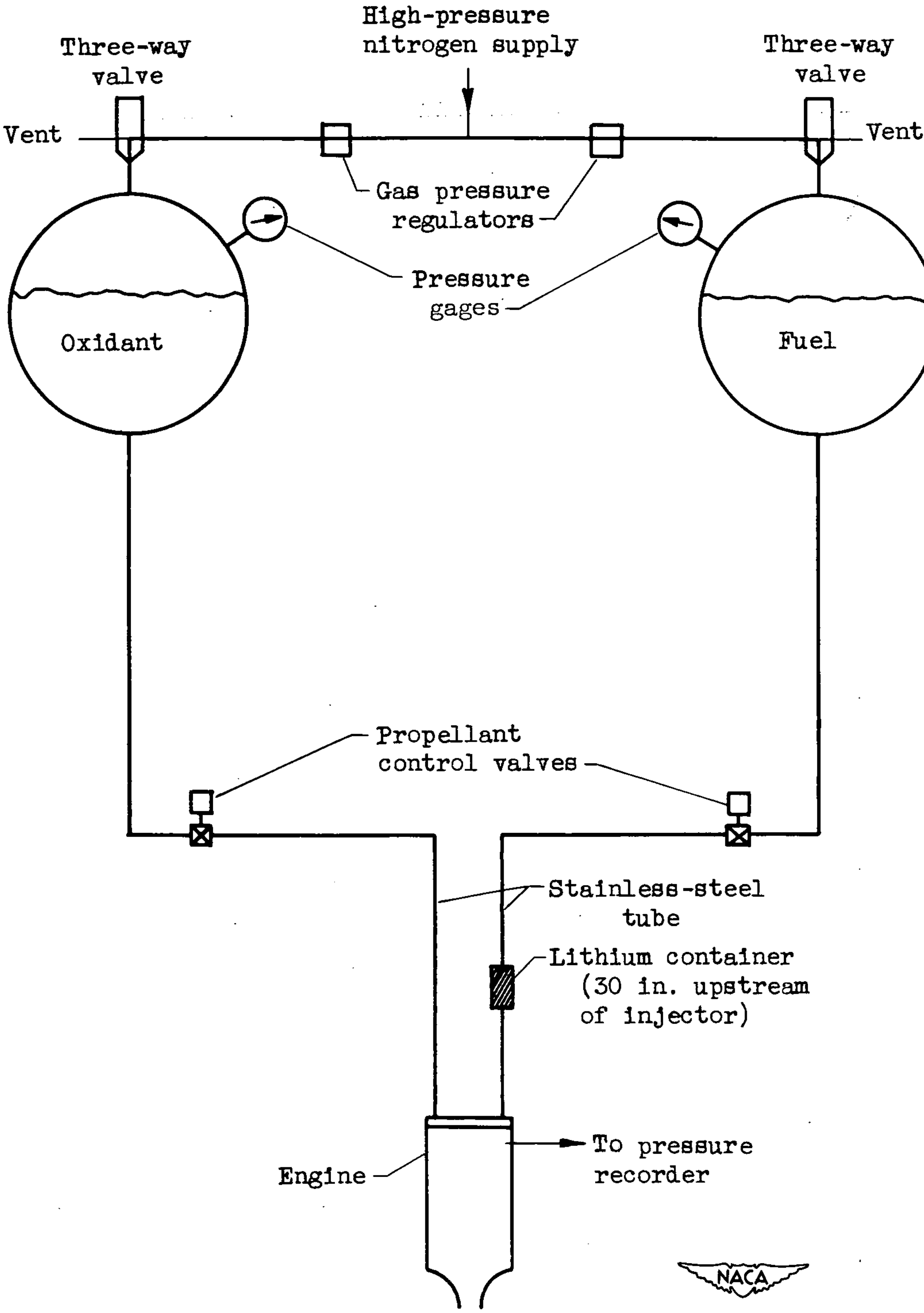

Figure 1. - Flow system for 100-pound-thrust engine.

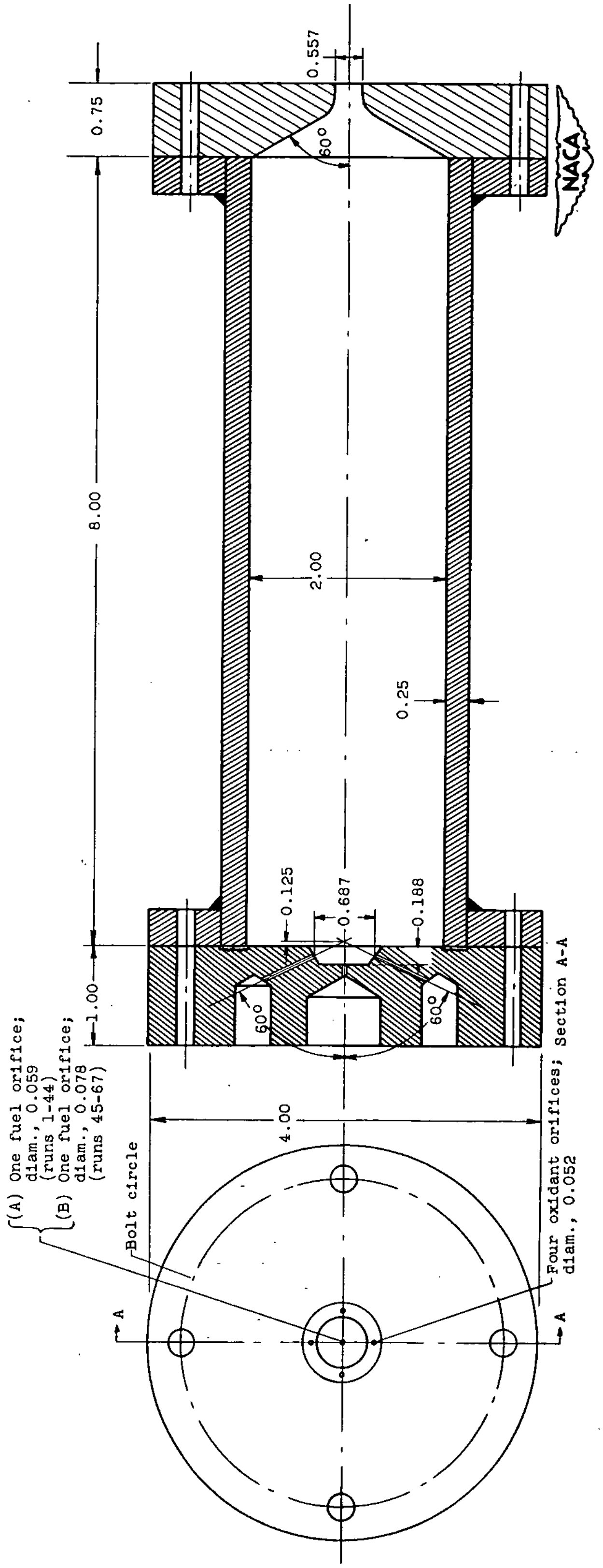

Figure 2. - Schematic diagram of 100-pound-thrust engine. (All dimensions are in inches.)

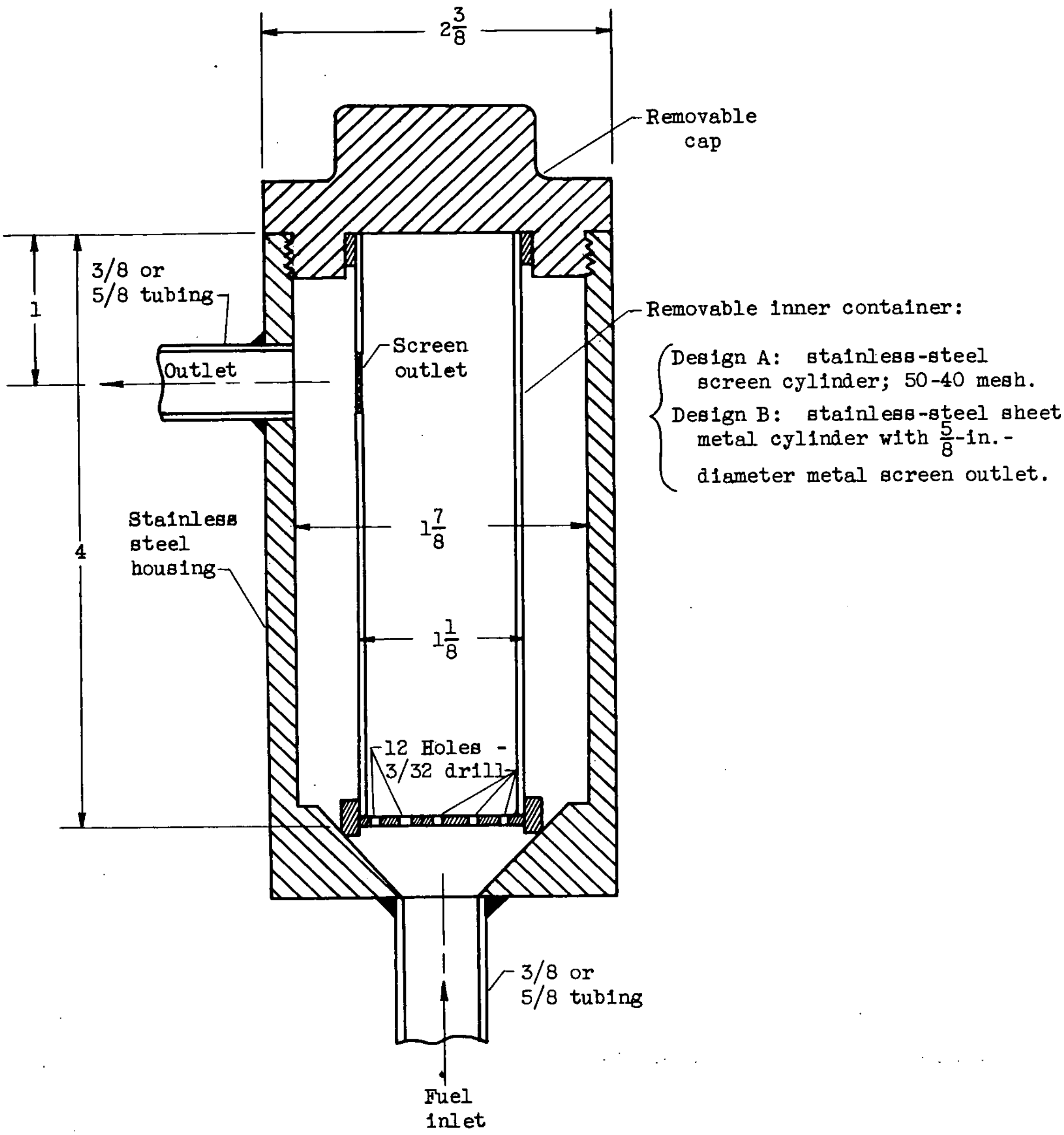

Figure 3. - Lithium container for 100- and 1000-pound-thrust engines. (All dimensions are in inches.)

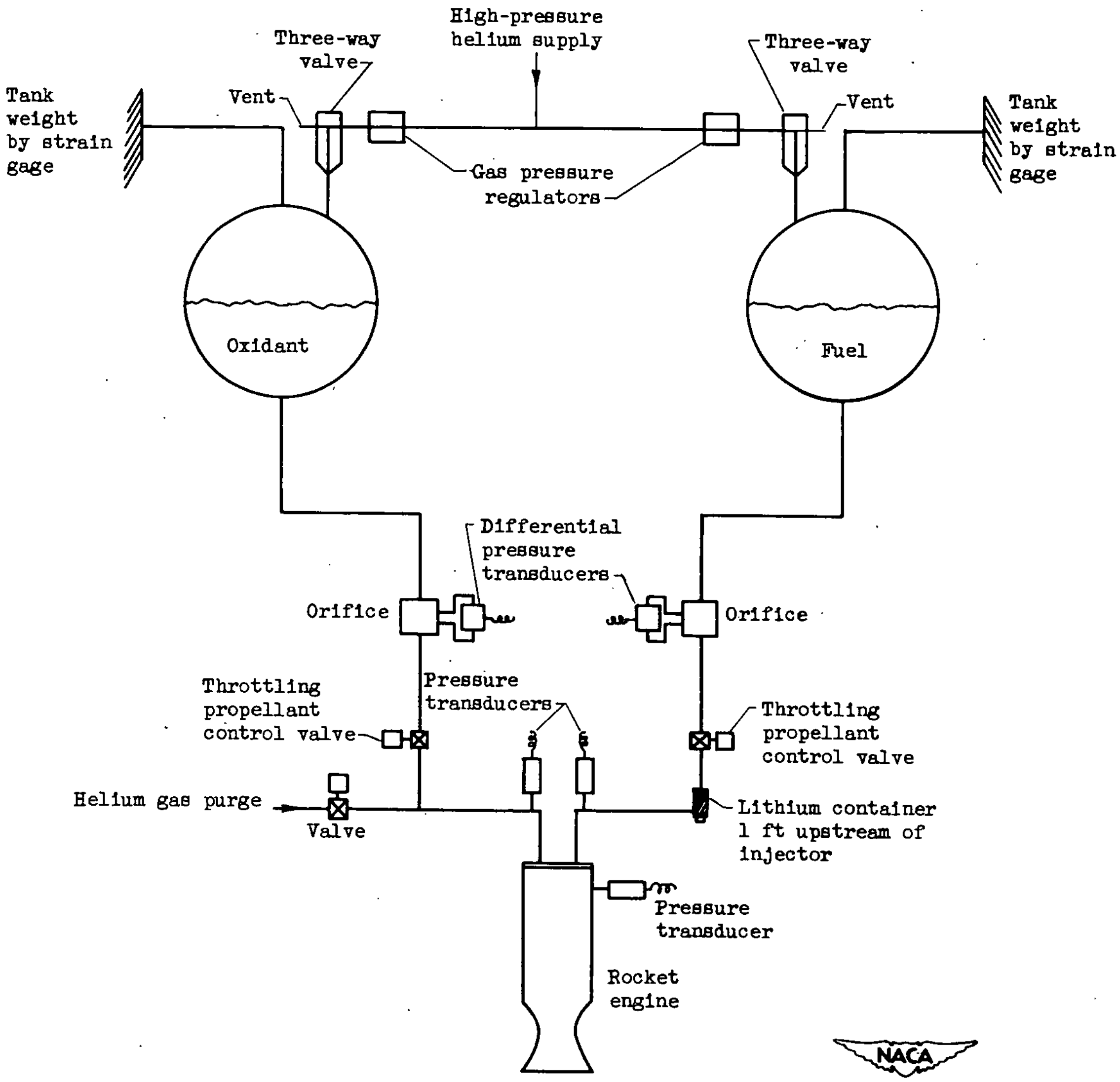

Figure 4. - Flow system for 1000-pound-thrust engine.

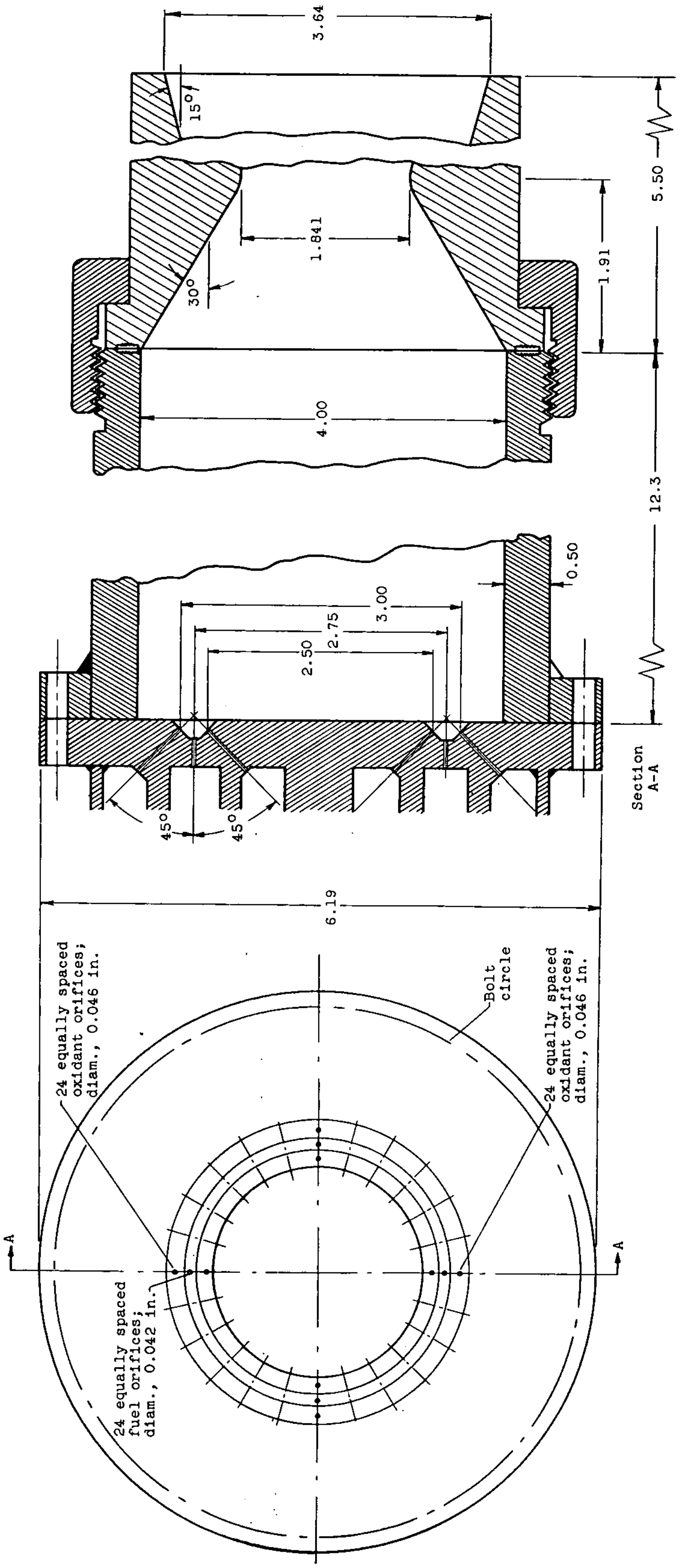

Figure 5. - Schematic diagram of 1000-pound-thrust engine. (All dimensions are in inches.)

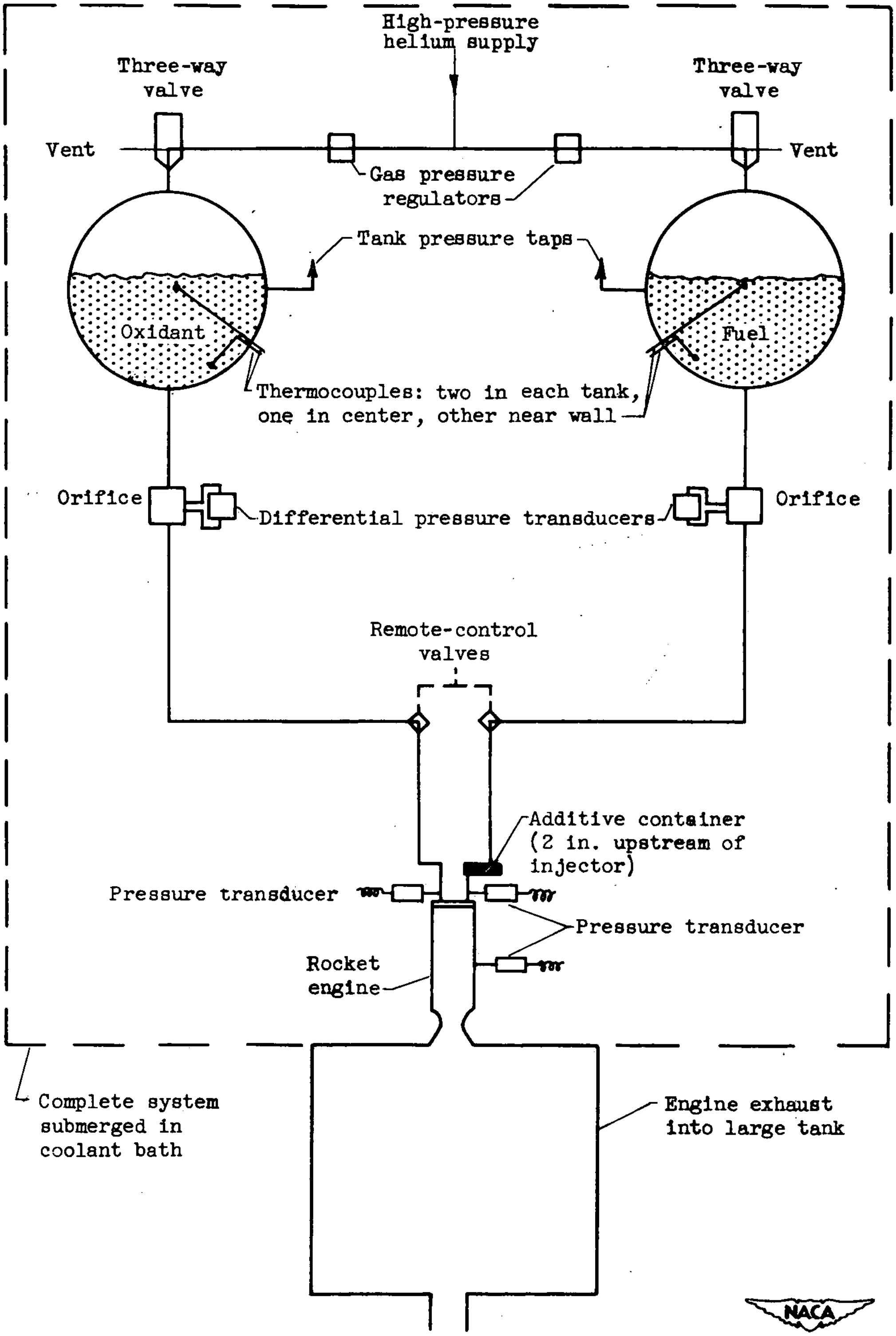

Figure 6. - Flow system for low-temperature experiments.

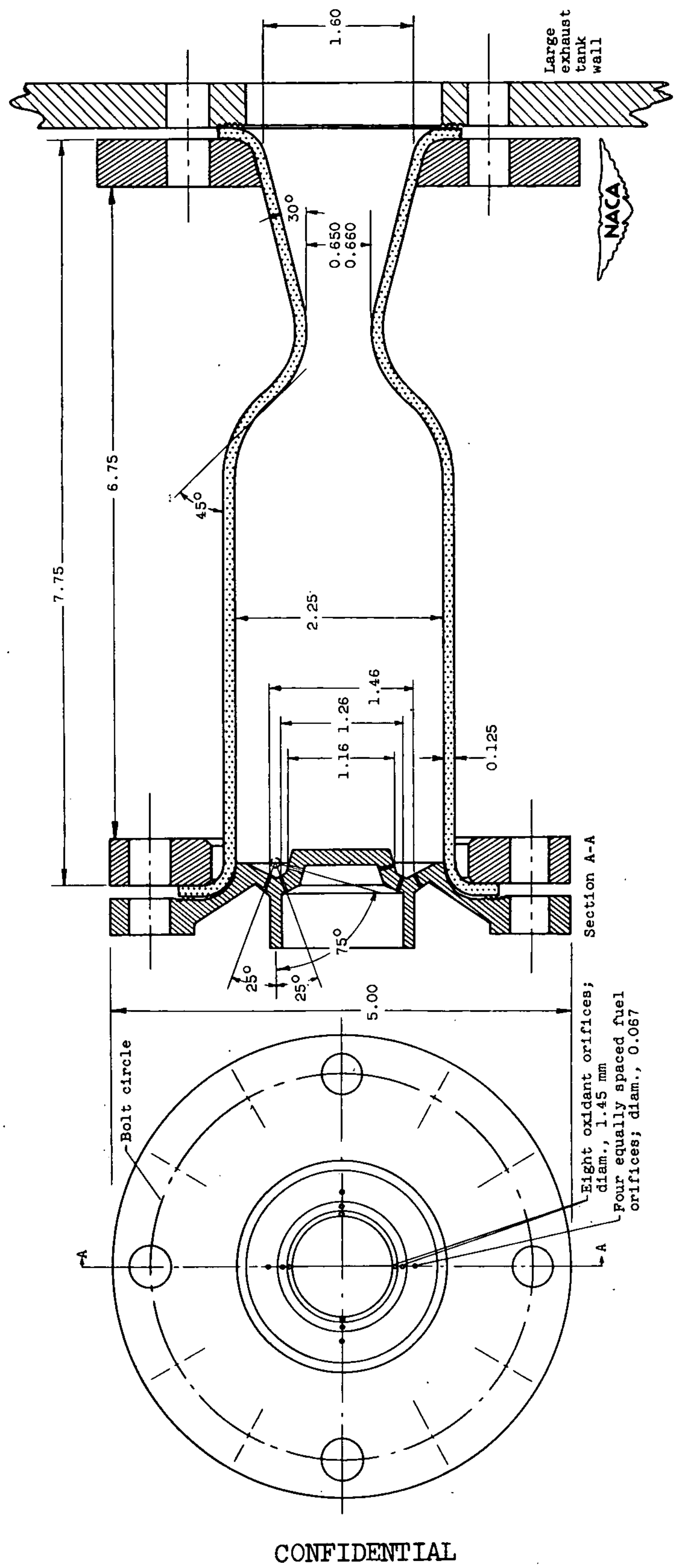

Figure 7. - Schematic diagram of 200-pound-thrust engine A. (All dimensions are in inches except where noted.)

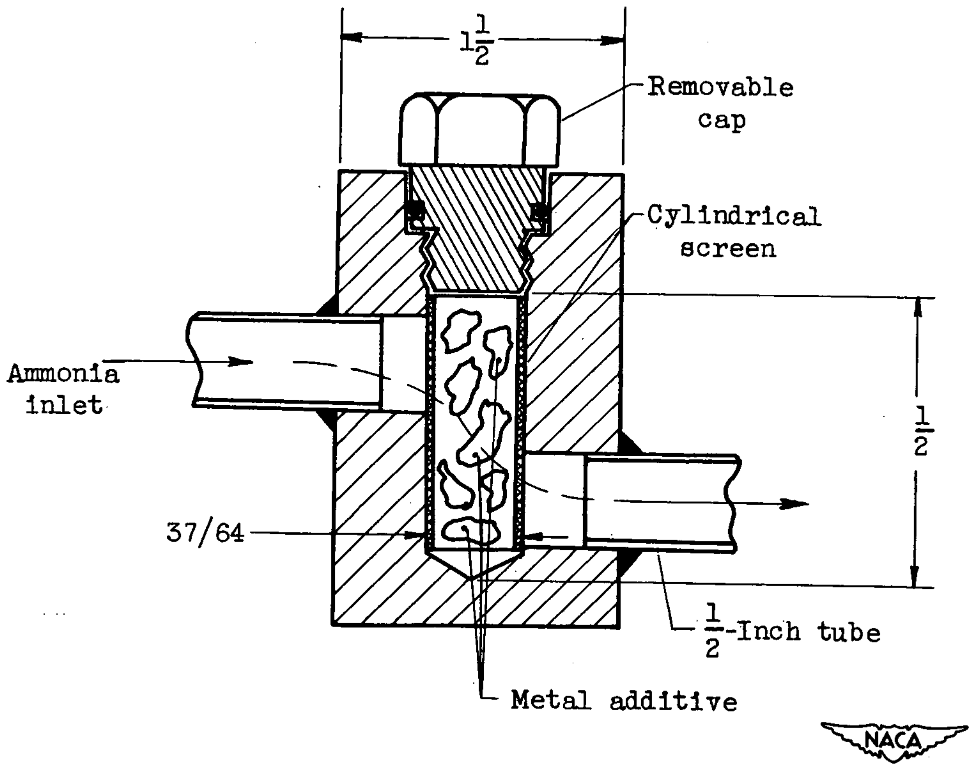

Figure 8. - Additive container for 200-pound-thrust engine. (All dimensions are in inches.)

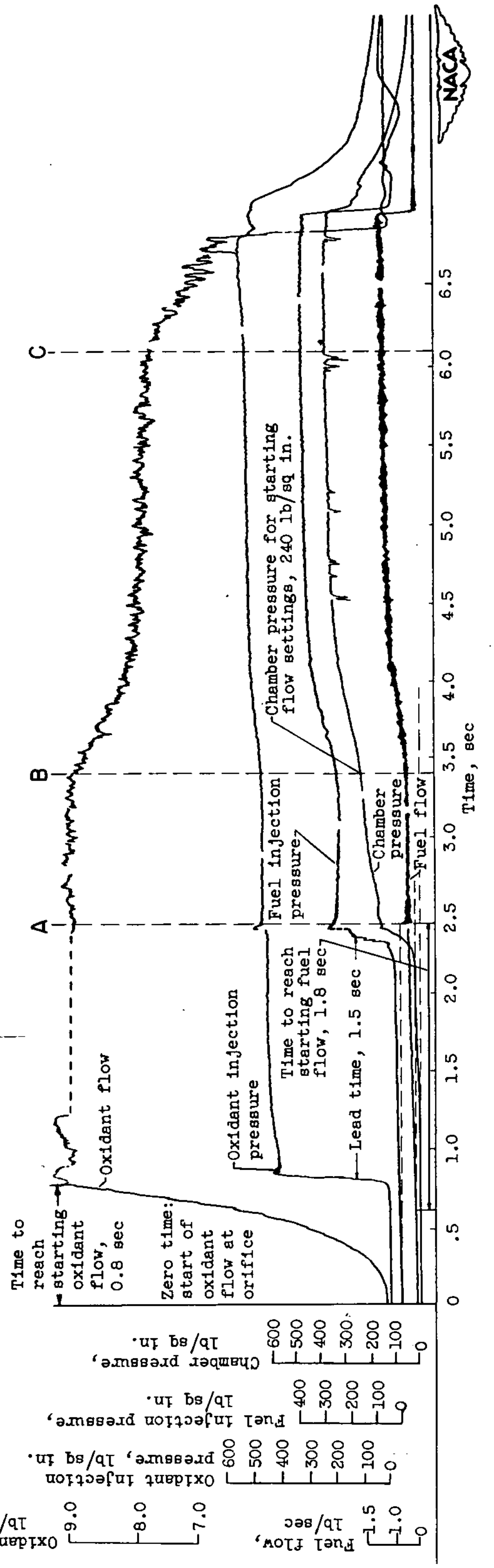

Figure 9. - Typical oscillograph-time record of propellant flows and injection and chamber pressures for 1000-pound-thrust engine. Run 8; oxidant lead time, 1.5 seconds. A, starting flow conditions: total flow, 9.6 pounds per second; oxidant-fuel weight ratio, 14. B, start of flow change to higher thrust. C, conditions after flow change: chamber pressure, 368 pounds per square inch; flow, 9.2 pounds per second; oxidant-fuel weight ratio, 5.7.

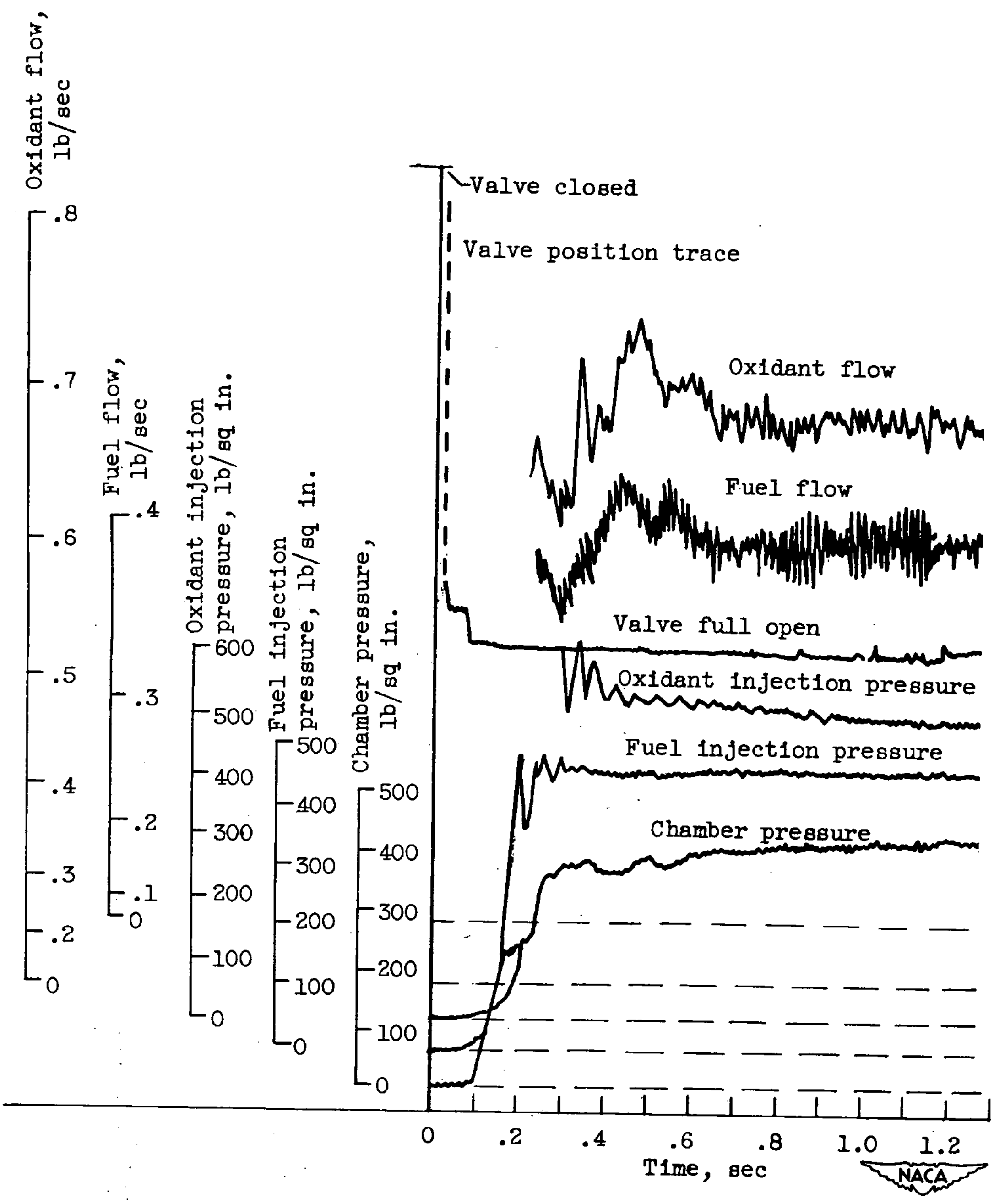

Figure 10. - Typical oscillograph-time record of propellant flows and injection and chamber pressures for 200-pound-thrust engine at -85° F. Run 2; oxidant-fuel weight ratio, 1.4.